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Effects of thermal pre-treatment and recuperative thickening on the fate of trace organic contaminants during anaerobic digestion of sewage sludge

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Effects of thermal pre-treatment and recuperative thickening on the fate of trace organic contaminants during anaerobic digestion of sewage sludge

Abstract

This study examined the effects of thermal pre-treatment and recuperative thickening on anaerobic digestion of sewage sludge on biogas production and removal of trace organic contaminants (TrOCs). Thermal pre-treatment and recuperative thickening resulted in approximately 15% increase in biogas production. However, the effects of thermal pretreatment and recuperative thickening on anaerobic digestion performance in respect to the removal of TrOCs were less obvious and varied widely depending on the molecular properties of each compound. Of the 40 TrOCs monitored in this study, 16 TrOCs were detected in all primary sludge samples. Removal from the aqueous phase was negligible for most of these 16 TrOCs. Caffeine and paracetamol were the only two TrOCs with a high removal from the aqueous phase. In comparison to the aqueous phase, TrOC removal from the solid phase was considerably higher. Through a mass balance calculation, it was shown that thermal pre-treatment or a combination of thermal pre-treatment and recuperative thickening could enhance the biodegradation of five persistent TrOCs, namely TCEP, verapamil, clozapine, triclosan, and triclocarban by 17-50%.

Disciplines

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17 **Abstract:** This study examined the effects of thermal pretreatment and recuperative
18 thickening on anaerobic digestion of sewage sludge on biogas production and removal of
19 trace organic contaminants (TrOCs). Thermal pre-treatment and recuperative thickening
20 resulted in approximately 15% increase in biogas production. However, the effects of thermal
21 pretreatment and recuperative thickening on anaerobic digestion performance in respect to
22 the removal of TrOCs were less obvious and varied widely depending on the molecular
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25 paracetamol were the only two TrOCs with a high removal from the aqueous phase. In
26 comparison to the aqueous phase, TrOC removal from the solid phase was considerably
27 higher. Through a mass balance calculation, it was shown that thermal pre-treatment or a
28 combination of thermal pre-treatment and recuperative thickening could enhance the
29 biodegradation of five persistent TrOCs, namely TCEP, verapamil, clozapine, triclosan, and
30 triclocarban by 17 to 50%.

31 **Keywords:** Anaerobic digestion, thermal pre-treatment, recuperative thickening, biogas,
32 traces organic contaminants, biodegradation.

33

34 **1. Introduction**

35 Urbanization and continuous population growth have imposed an increasing demand on
36 wastewater treatment plants (WWTPs) particularly in regard to the management of sewage
37 sludge. In Australia, sewage sludge production (as dried solids) has increased from 0.30 to
38 0.33 million tonnes between 2010 to 2013 (Semblante et al., 2014). Sewage sludge contains
39 biodegradable organics and an array of pathogens. Thus, sewage sludge treatment is
40 necessary before any beneficial use or land disposal. Anaerobic digestion is currently the
41 most widely used technique for sewage sludge treatment. Anaerobic digestion is a biological
42 process in which microorganisms convert biodegradable materials in the absence of oxygen
43 to biogas and more stable organics. It is well established that anaerobic digestion can
44 efficiently stabilise organic materials and remove pathogenic agents in sewage sludge while
45 simultaneously producing valuable biogas (Sawatdeenarunat et al., 2016; Sihuang et al., 2016;
46 Tuyet et al., 2016). Biogas is a form of renewable fuel, which can be used to generate
47 electricity and heat (Nghiem et al., 2017). The remaining and more stable solids are rich in
48 nutrient and organics, thus, can be used for soil amendment (Nghiem et al., 2017).

49 Anaerobic digestion consists of four stages with hydrolysis being the first during which
50 organic materials are transformed to fatty acids and other soluble organic compounds (Habiba
51 et al., 2009). Since hydrolysis is the rate limiting step during anaerobic digestion, several pre-
52 treatment methods, including thermal hydrolysis, biological treatment, ultrasonication, and
53 ozonation, have been suggested to increase the digestion rate or improve the inherent
54 degradability of sewage sludge (Carrère et al., 2010; Dhar et al., 2012). Thermal hydrolysis is
55 a promising pre-treatment method to improve methane production during anaerobic
56 processing ([Supplementary data Table S1](#)) since complex organic molecules can be
57 transformed into short-chain fragments better suited for biological digestion (Liao et al.,
58 2016; Mottet et al., 2009; Schieder et al., 2000). The effects of thermal pre-treatment at

59 temperature of up to 180 °C and duration up to 2 hours on anaerobic digestion performance
60 have been evaluated by several recent studies (Bougrier et al., 2008; Kim et al., 2003; Pérez-
61 Elvira and Fdz-Polanco, 2012; Phothilangka et al., 2008; Valo et al., 2004). The optimal
62 temperature of thermal hydrolysis was reported to be 150-180 °C by Bougrier et al. (2008)
63 for a pre-treatment duration of 30 to 60 minutes. Thermal hydrolysis has been successfully
64 used at a full scale wastewater treatment plant (Kepp et al., 2000). The energy balance
65 calculation showed the net electricity production due to enhanced biogas production
66 increased by over 20%, which is more than the energy input for thermal hydrolysis.

67 In addition to thermal pre-treatment, recuperative thickening has also been identified as a
68 potentially cost-effective and readily implementable method to improve anaerobic digester
69 performance without the need to increase the size of the digester (Cobbledick et al., 2016).
70 Recuperative thickening can increase the solids retention time (SRT) independently of the
71 hydraulic retention time (HRT) by thickening a proportion of the digestate to remove water
72 and then returning the thickened sludge back to the digester (Reynolds et al., 2001; Torpey
73 and Melbinger, 1967; Yang et al., 2015). The increase in SRT helps to improve the
74 conversion of organics to methane and increase the volatile solid (VS) reduction (Sieger et al.,
75 2004; Yang et al., 2015). Recuperative thickening has been successfully applied in a few
76 WWTPs in North America and Australia. Full scale monitoring data suggest that recuperative
77 thickening can improve both biogas production and VS reduction by 15-30% (Greer, 2011;
78 Reynolds et al., 2001).

79 A major issue associated with beneficial reuse of reclaimed water and biosolids from sewage
80 treatment is the ubiquitous occurrence of trace organic contaminants (TrOCs) in municipal
81 wastewater. These TrOCs include several groups of widely used compounds including
82 pharmaceuticals and personal care products, steroid hormones, industrial chemicals,
83 pesticides, phytoestrogens, and UV filters. Their toxicological effects on human and other

84 biota even at a very low concentration (less than 1 µg/L) remain largely unknown but are
85 generally suspected (Luo et al., 2014). Some TrOCs can partition from the aqueous phase in
86 wastewater to the solid phase in sludge during wastewater treatment (Citulski and
87 Farahbakhsh, 2010; Semblante et al., 2015). When applied to farm land, these TrOCs may
88 accumulate in soil, presenting a potential risk to human health and the ecosystem (Citulski
89 and Farahbakhsh, 2010). However, to date, there have been only a few investigations on the
90 removal of TrOCs from sewage sludge by anaerobic treatment.

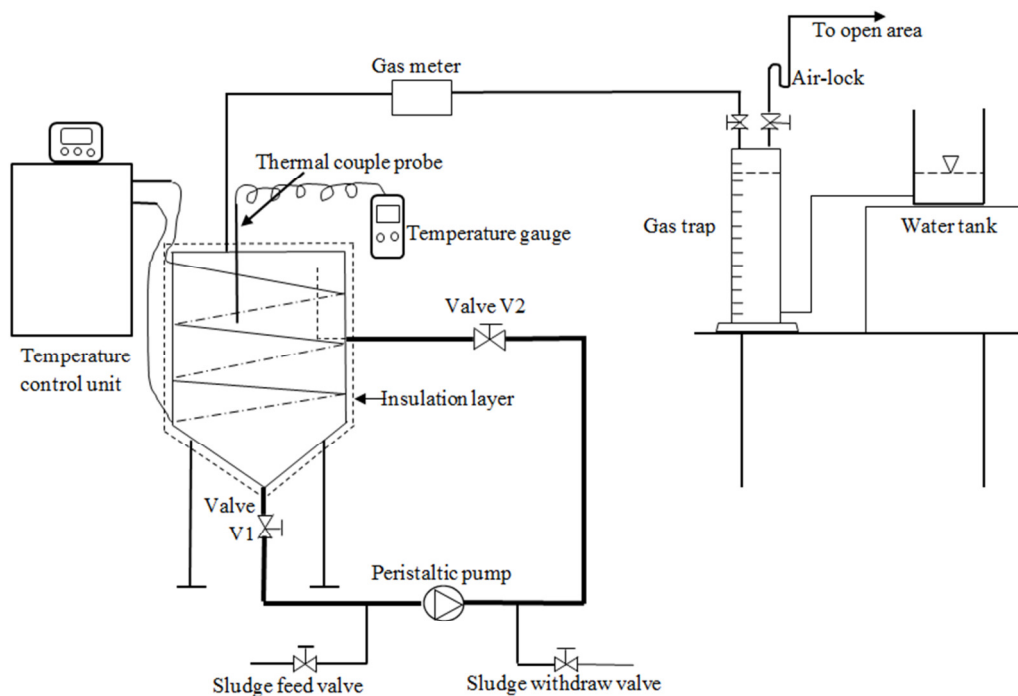
91 Of a particular note, little is known about the impact of pre-treatment on the removal of
92 TrOCs from sewage sludge by anaerobic digestion. In a systematic lab-scale study,
93 McNamara et al. (2012) observed no discernible impact of thermal hydrolysis on the
94 degradation of nonylphenol ethoxylates by anaerobic digestion. Similarly, Carballa et al.
95 (2006) reported that thermal pre-treatment of sewage sludge had no observable impact on the
96 removal of several pharmaceuticals, musks, and steroid hormones. By contrast, Hamid and
97 Eskicioglu (2013) observed a notable increase in the removal of estrone and estradiol by
98 anaerobic treatment following microwave-assisted pre-treatment (80 to 160 °C, 2.45 GHz,
99 1200 W). Given the paucity of information on this important issue, the present study aims to
100 evaluate the influence of thermal hydrolysis and recuperative thickening on the fate of TrOCs
101 in sewage sludge during anaerobic digestion. The influence of thermal hydrolysis and
102 recuperative thickening on anaerobic digestion performance in terms of biogas production
103 and organics removal is also investigated.

104 **2. Materials and Methods**

105 **2.1 Lab-scale anaerobic digester and sludge**

106 Three lab-scale anaerobic digesters previously described by Yang et al. (2016) were used in
107 this study (Fig 1). Briefly, each digester consisted of a 28 L stainless steel reactor (Core

108 Brewing Concepts, Victoria, Australia), a peristaltic hose pump (DULCO®flex from
 109 ProMinent Fluid Controls, Australia), a temperature control unit (Neslab RTE 7), a thermal
 110 couple with temperature gauge, a biogas counter, and a gas trap for biogas sampling. One
 111 digester (denoted as D1) was operated as the control system without thermal pre-treatment
 112 and recuperative thickening. One digester (denoted as D2) was operated with thermal pre-
 113 treatment. The last reactor (denoted as D3) was operated with both thermal pre-treatment and
 114 recuperative thickening. All three reactors were operated in parallel and were each seeded
 115 with 20 L anaerobically digested sludge. The digested sludge and primary sludge were all
 116 sampled from a full scale wastewater treatment plant in New South Wales, Australia, with
 117 average total solid (TS) content of 29.0 ± 1.0 g/L and 22.2 ± 2.2 g/L, respectively. All sludge
 118 samples were stored at 4 °C until use or else discarded within two weeks.



119

120 **Fig 1:** The schematic diagram of the three lab-scale anaerobic digesters.

121 All anaerobic digesters were operated under the same HRT of 20 d by wasting 1 L of
 122 digestate and the feeding with 1 L of primary sludge each day. Raw sludge, thermally

123 pretreated sludge, and digested sludge were collected weekly for characterisation. Parameters
124 that were regularly measured include TS, volatile solid (VS), chemical oxygen demand
125 (COD), alkalinity and pH.

126 **2.2 Thermal pre-treatment**

127 The feed sludge to digester D2 and D3 was thermally pretreated at 150 °C and 500 kPa for 30
128 minutes using a New Tek Machinery pressure vessel (Changzhou, China) with a heating
129 jacket. At the conclusion of the process, the pressure inside the vessel was released and the
130 sludge was allowed to cool to room temperature (ca. 25 °C) before feeding to the digester.

131 **2.3 Recuperative thickening**

132 *Digester D3 was operated with recuperative thickening to achieve an SRT of 30 d with the*
133 *HRT at 20 d i.e., same as the other digesters. A thickening ratio of 1.33 (which is the ratio of*
134 *the total TS from primary sludge feed and return thickened sludge over the TS from primary*
135 *sludge feed) was used.* Each day, 2 L of the digestate was withdrawn from digester D3 and
136 dosed with thickening polymer (Zetag 8169, BASF) at 7.5 g/Kg dry sludge. The sludge was
137 gently mixed and allowed to settle by gravity for at least 10 minutes. 1 L of thickened sludge
138 was then mixed with the thermally pretreated (150 °C, 30 min) primary sludge (1 L) to form
139 2 L of feed to return to the digester. The excess thickened sludge and supernatant were
140 discarded.

141 **2.4 Analytical methods**

142 2.4.1 Anaerobic digestion performance

143 Biogas production rate was monitored daily by a custom-made gas counter (Yang et al.,
144 2016). The biogas composition was detected weekly by a portable gas analyser (GA5000 gas
145 analyser, Geotechnical Instruments Ltd, UK) (Nghiem et al., 2014). Additionally, samples

146 from primary sludge (before and after thermal treatment) and digested sludge were taken
147 weekly to analyse sludge characters such as TS, VS, total COD (tCOD), soluble COD
148 (sCOD), pH and alkalinity. TS, VS, and alkalinity were measured in accordance to the
149 standard methods. COD was measured following the US-EPA Method 8000 using high range
150 plus COD vials (HACH, USA). The supernatant used for measurement of sCOD was
151 obtained by centrifuging sludge sample at 3720xg for 10 minutes (Allegra X-12R centrifuge,
152 Beckman Coulter, Australia), and then filtering through 1 μm glass microfiber filter paper
153 (Filtech, Australia).

154 2.4.2 TrOC sample preparation and analysis

155 Primary and digested samples were collected every 7 days to prepare duplicate samples for
156 TrOC concentration analysis (Wijekoon et al., 2015). Sludge samples were centrifuged at
157 3720xg for 10 minutes (Allegra X-12R, Beckman Coulter, USA) to obtain solid pellets and
158 supernatant for further processing. Supernatant from sludge sample (50 mL) was diluted with
159 Milli-Q to 500 mL. Then the obtained aqueous samples were filtered by 1 μm and then 0.7
160 μm pore size glass fiber filter paper. The filtered samples were spiked with surrogate (50 μL
161 per sample) containing 40 isotopically labelled standards for method recovery and determine
162 TrOC concentration before proceeding to solid phase extraction (SPE). During the SPE, HLB
163 cartridges were conditioned with 5 mL methyl tert-butyl ether, 5 mL methanol, and 2 x 5 mL
164 Milli-Q water before the liquid samples were loaded to the cartridges at the flow rate of
165 approximately 15 mL/min. After concentrating to 1 mL, eluted samples were subjected to
166 high performance liquid chromatography-tandem mass spectrometry analysis (HPLC-MSMS)
167 (Alturki et al., 2013). In this study, a spectrum of 40 TrOCs was used to prepare the surrogate
168 and screen the TrOC concentration of sludge samples.

169 The solid pellets were freeze-dried using an Alpha 1-2 LDplus Freeze dryer (Christ GmbH,
170 Germany). The dried samples were ground to powder and 0.5 g was transferred to a 13 mL
171 glass vial (with cap) for extraction. Methanol (10 mL) was added to the vial, mixed with the
172 powder by a vortex mixer (VM1, Ratek, Australia), and ultrasonicated for 10 minutes at
173 40 °C. The solution was then centrifuged at 3720xg for 10 minutes to obtain a supernatant.
174 The residual solid was extracted using 10 mL solvent made of dichloromethane and methanol
175 (1:1, v/v) by repeating the previous steps. The supernatants from these steps were combined
176 and diluted to 500 mL by Milli-Q water. The liquid samples were then filtered, spiked with
177 surrogate, loaded to the SPE cartridges and analysed following the same procedure for sludge
178 supernatant samples described before.

179 2.4.3 TrOC mass balance

180 Mass balance calculations were conducted for each TrOC to determine their fate in the
181 aqueous and solid phase (Wijekoon et al., 2015). The total mass of each TrOC fed into the
182 system can be described as:

$$183 \quad M_{in} = X_{in} \times TS_{PS} + S_{in} \quad (1)$$

184 where M_{in} is the total mass of TrOC in 1 L of feed (ng), X_{in} is the TrOC concentration in the
185 solid phase of primary sludge (ng/g dry sludge), TS_{PS} is the total solid concentration of
186 primary sludge (g/L), and S_{in} is the TrOC concentration in the aqueous phase of primary
187 sludge (ng/L). The mass of TrOC (M_{aq}) in the aqueous phase in 1 L of the digestate can be
188 measured experimentally. The mass of TrOC in the solid phase of the digestate can be
189 described as:

$$190 \quad M_{solid} = X_{solid} \times TS_{DS} \quad (2)$$

191 where M_{solid} is the mass of TrOC in the solid phase (ng), X_{solid} is the TrOC concentration in
192 the solid phase of digested sludge (ng/g dry sludge), TS_{DS} is the total solid concentration of
193 digested sludge (g/L). Thus the mass balance for TrOC concentration can be presented as

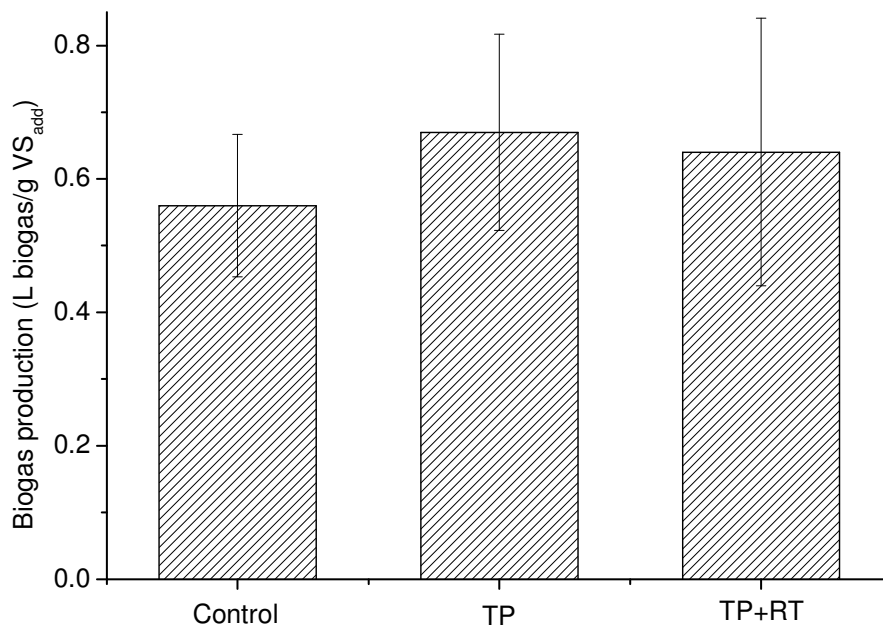
$$194 \quad M_{in} = M_{aq} + M_{solid} + M_{bio} \quad (3)$$

195 where M_{bio} is the mass of TrOC that has been biodegraded.

196 **3. Results and discussion**

197 **3.1 Thermal pre-treatment and recuperative thickening**

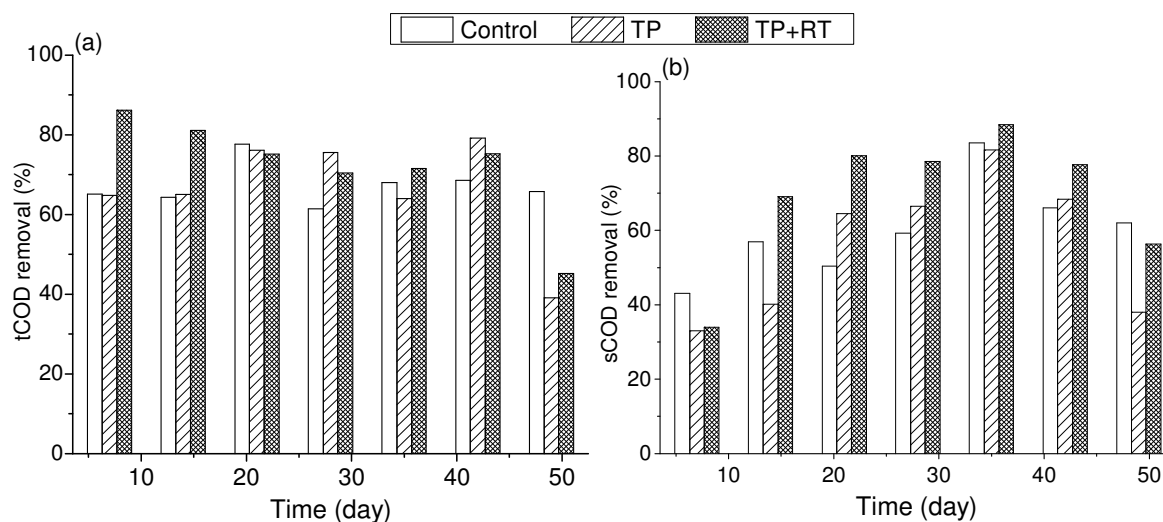
198 Thermal pre-treatment and recuperative thickening (Digester D3) resulted in approximately
199 15% increase in biogas production in comparison to the control digester (D1) (Fig 2). The
200 combination of thermal pre-treatment and recuperative thickening (Digester D3) did not lead
201 to any additional increase in biogas production compared to only thermal pre-treatment (D2).
202 According to Pilli et al., (2015), thermal pre-treatment causes the disintegration and
203 solubilisation of some solid sludge particles, thus, enhancing the hydrolysis step and hence
204 biogas production. Indeed, in this study, in which approximately 10% of the tCOD of primary
205 sludge was converted to sCOD after thermal treatment. On the other hand, recuperative
206 thickening can extend the residence time of sludge in the reactor and recapture soluble
207 macro-organic molecules for further digestion. Biogas production-increase by up to 30% has
208 been reported in previous laboratory scale and full scale studies (Cobbledick et al., 2016;
209 Reynolds et al., 2001). Results from Fig 2 suggest that the benefits of thermal pre-treatment
210 and recuperative thickening are mutually exclusive. It is also noteworthy that thermal pre-
211 treatment and recuperative thickening did not exert any observable impact on biogas
212 composition. Throughout this study, biogas composition from all three digesters was stable
213 with approximately 60% CH₄ and 40% CO₂.



214

215 **Fig 2:** Average biogas production from digester D1 (Control), D2 (Thermal pre-treatment
 216 (TP)) and D3 (Thermal pre-treatment and recuperative thickening (TP+RT)). Error bars show
 217 the standard deviation of 7 measurements (one per week).

218 The sludge composition varied quite significantly throughout the course of this study. Since
 219 organic removal in terms of TS, VS, tCOD and sCOD was determined on a weekly basis,
 220 there were some notable variations. TS and VS removals ranged from 50 to 80% and 70 to
 221 90%, respectively. Due to these significant variations in TS and VS, the effects of thermal
 222 pre-treatment and recuperative thickening were not observable in this study. Nevertheless,
 223 some enhancement in the removal of tCOD and sCOD could be observed in Fig 3. With the
 224 exception of day 49, the removal of tCOD by Digester 2 (thermal pre-treatment) and Digester
 225 3 (thermal pretreatment and recuperative thickening) was comparable or higher than that of
 226 the control digester (Fig 3a).



227

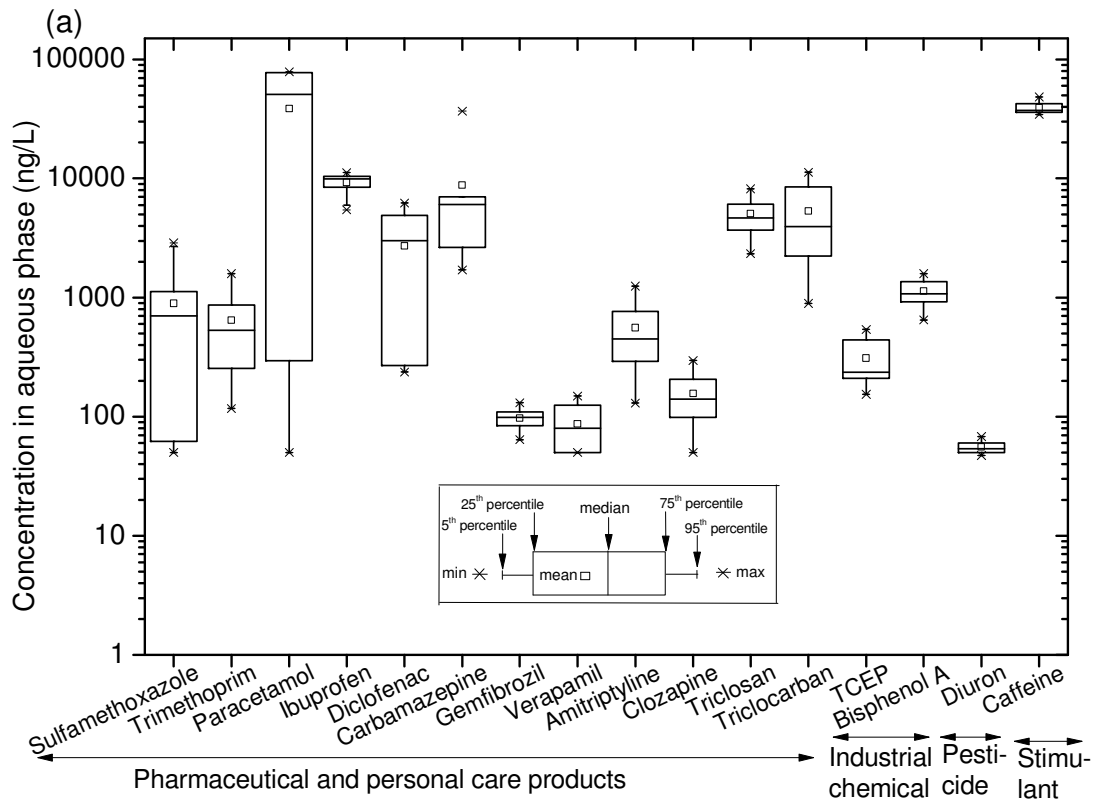
228 **Fig 3:** (a) tCOD removal and (b) sCOD removal by the control digester (D1), digester 2 with
 229 thermal pre-treatment (TP), and digester 3 with thermal pre-treatment and recuperative
 230 thickening (TP+RT).

231 The effect of pre-treatment and recuperative thickening on removal performance was most
 232 notable in terms of sCOD removal. Digester D2 showed comparable sCOD removal to that
 233 by the control digester (D1). On the other hand, digester D3 showed a notable increase in
 234 sCOD removal (Fig 3b). As noted above, thermal pre-treatment led to the solubilisation of
 235 some tCOD into sCOD. On the other hand, due to sludge thickening, soluble organics can be
 236 retained for further digestion. Thus, recuperative thickening could improve the removal of
 237 sCOD.

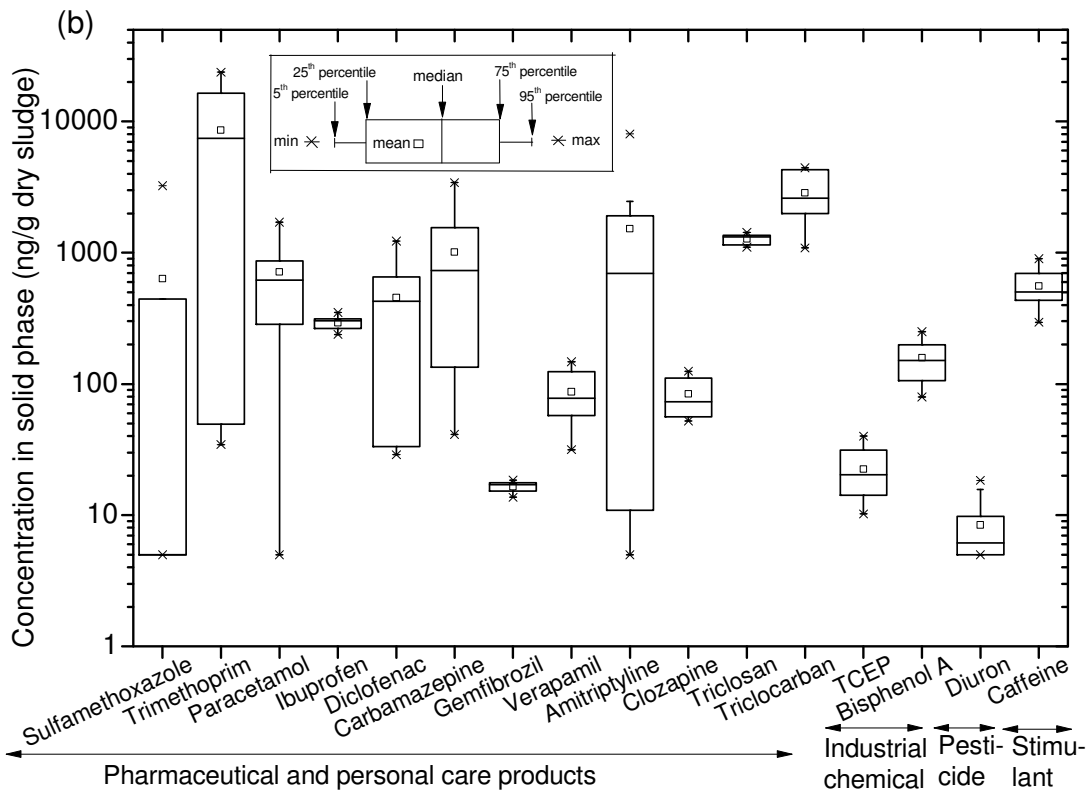
238 Several other parameters including pH and alkalinity were also monitored. The mixed liquor
 239 pH value of all three digesters was stable between 7.0 – 7.5 and the alkalinity was over 2600
 240 mg CaCO₃/L (Supplementary data Fig S4). These results confirm stable operation of all three
 241 digesters in this study.

242 3.2 TrOC occurrence in primary sludge

243 In good agreement with a previous study by Yang et al. (2017), of the 40 TrOCs monitored in
244 this study, 16 compounds were prevalently detected in all primary sludge samples (Fig 4).
245 The concentrations in the aqueous and solid phase were in the range from 50 to 40,000 ng/L
246 and from 20 to nearly 9,000 ng/g dry sludge, respectively. The occurrence of these TrOCs in
247 primary sludge is well related to their usage in daily life. For examples, caffeine (which is a
248 stimulant in coffee and tea) and paracetamol (which is a widely used pain killer) were
249 detected at the highest concentration in the aqueous phase (40,000 and 38,000 ng/L,
250 respectively). At the TS content of 29 g/L, it can also be inferred from Fig 4 that these TrOCs
251 occurred mostly in the solid phase (i.e. 70 to 100% in the total mass in primary sludge).
252 Caffeine and ibuprofen are the only two exceptions. The mass distributions of caffeine and
253 ibuprofen in the solid phase were 24 and 41%, respectively, possibly because of their
254 hydrophilicity. These results highlight the need for specific investigation of the removal of
255 TrOCs from the solid phase and that data from previous studies considering only the aqueous
256 phase may not be valid in the context of anaerobic digestion.



257



258

259 **Fig 4:** TrOC concentrations in (a) aqueous phase and (b) solid phase of primary sludge. 12

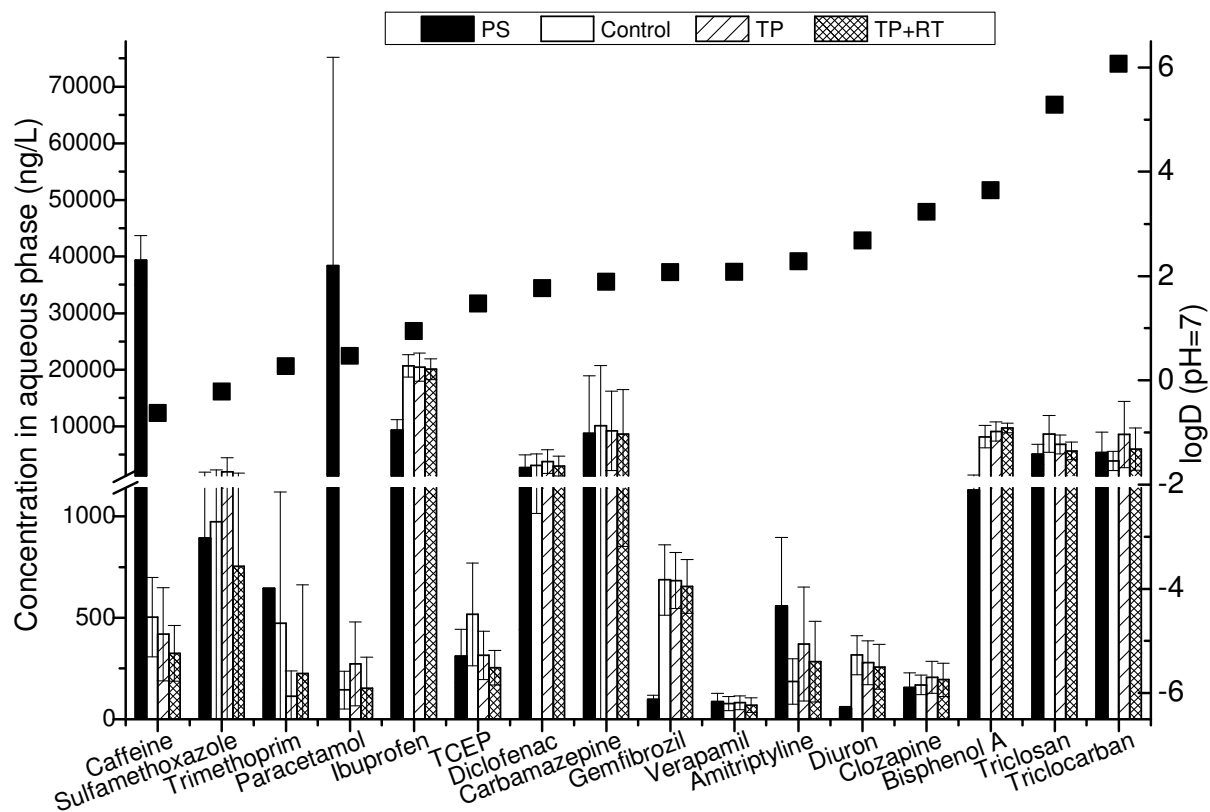
260 samples were taken during the experimental period.

261 3.3 TrOC removal in the aqueous and solid phase

262 TrOC concentrations in the aqueous and solid phase of the feed and digestate from the three
263 reactors are shown in Figs. 4 and 5, respectively. In these Figs, the TrOCs were listed in the
264 order of increasing hydrophobicity. Under all experimental conditions, caffeine and
265 paracetamol were almost completely removed (98 – 99%) from the aqueous phase (Fig 5).
266 Moderate removals from the aqueous phase were observed for trimethoprim and amitriptyline,
267 especially when pre-treatment and recuperative thickening were applied together (D3).
268 However, all other TrOCs were not significantly removed from the aqueous phase as can be
269 observed with all three digesters (Fig 5). In fact, in the case of ibuprofen, gemfibrozil, and
270 diuron, their concentrations in the aqueous phase of the digestate (after anaerobic treatment)
271 were even higher than the corresponding values of the feed primary sludge (Fig 5). It is
272 possible that the anaerobic condition could facilitate the transfer of some TrOCs from the
273 solid to aqueous phase. This is probably because of the transfer of TrOCs from the solid
274 phase to the aqueous phase during anaerobic digestion. It is also noteworthy from section 3.1
275 that most of these TrOCs are in the solid phase.

276 TrOC removal from the solid phase was notably higher in comparison to that from the
277 aqueous phase. As can be seen in Fig 6, several hydrophilic TrOCs including caffeine,
278 sulfamethoxazole, trimethoprim and paracetamol were well removed from the solid phase by
279 anaerobic digestion. The hydrophilicity of compounds appears to be an important factor for
280 their high removal from solid phase since hydrophilic compounds would easily desorb from
281 sludge granules. However, similar to the removal from aqueous phase, there is no obvious
282 evidence that thermal pre-treatment and recuperative thickening could improve the removal
283 of all of these TrOCs from the solid phase (Fig 6).

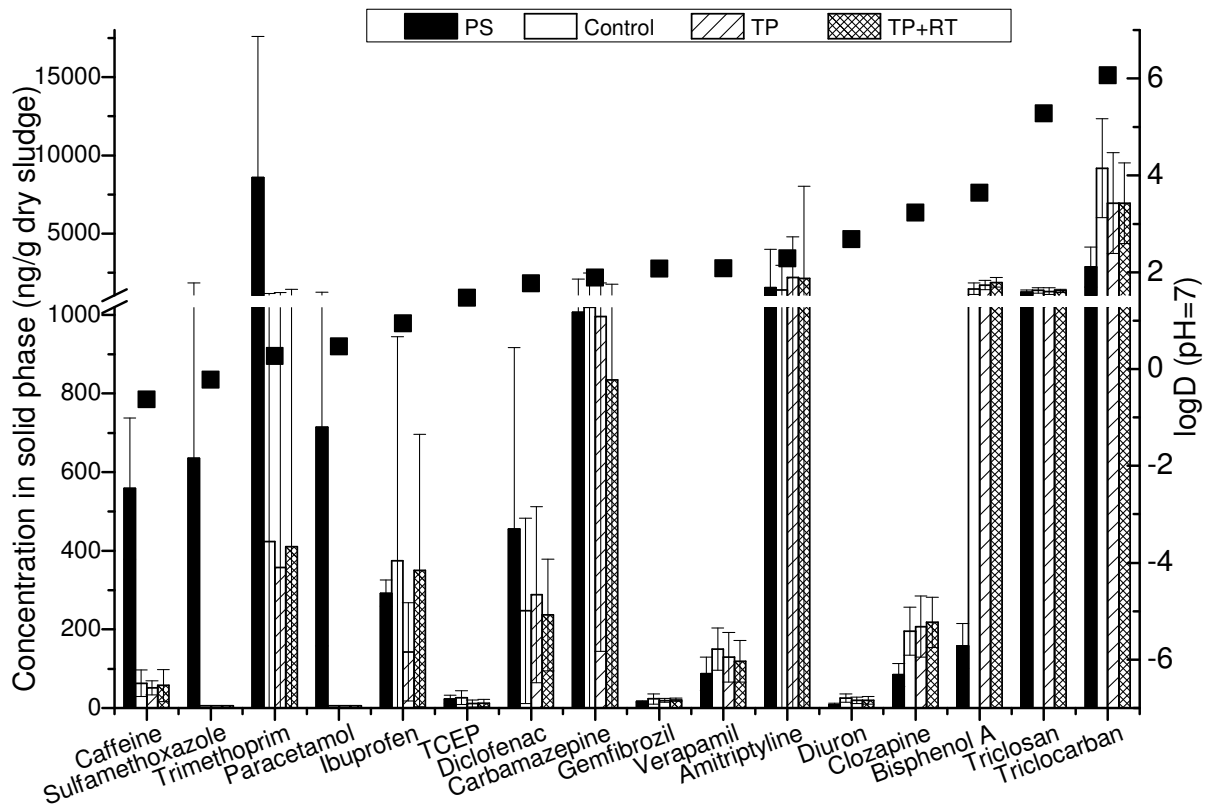
284



285
 286 **Fig 5:** Average concentrations of TrOCs in aqueous phase of primary sludge (PS), digested
 287 sludge from digester D1 (Control), D2 (TP) and D3 (TP+RT) (mean \pm standard deviation of
 288 12 samples).

289 Several previous studies have also shown no discernible changes in TrOC removal after
 290 thermal pre-treatment. For example, McNamara et al. (2012) reported that nonylphenol,
 291 diethoxylate and nonylphenol monoethoxylate were not removed from the influent by
 292 anaerobic treatment with and without thermal treatment (150 °C, 2 h). Similarly, Carballa et
 293 al. (2006) also reported that thermal pre-treatment of mixed sludge by autoclaving at 130 °C
 294 for 1 h had no impact on the removal of various pharmaceuticals, musks, and hormones by
 295 anaerobic treatment. However, it is noteworthy that these previous studies focused on the
 296 anaerobic treatment of wastewater and only considered the aqueous phase. Thus, their results
 297 cannot readily correlate to the anaerobic digestion of wastewater sludge. As discussed above,
 298 during anaerobic digestion of sludge, the transfer of TrOCs between the aqueous and solid

299 phase can influence the overall removal efficiency. Thus, it is important to conduct a mass
 300 balance to elucidate the contribution of biodegradation and the fate of TrOCs in the aqueous
 301 and solid phase.



302 **Fig 6:** Average concentrations of TrOCs in solid phase of primary sludge (PS), digested
 303 sludge from digester D1 (Control), D2 (TP) and D3 (TP+RT) (mean \pm standard deviation of
 304 12 samples).
 305

306 3.4 Fate of TrOCs during anaerobic digestion

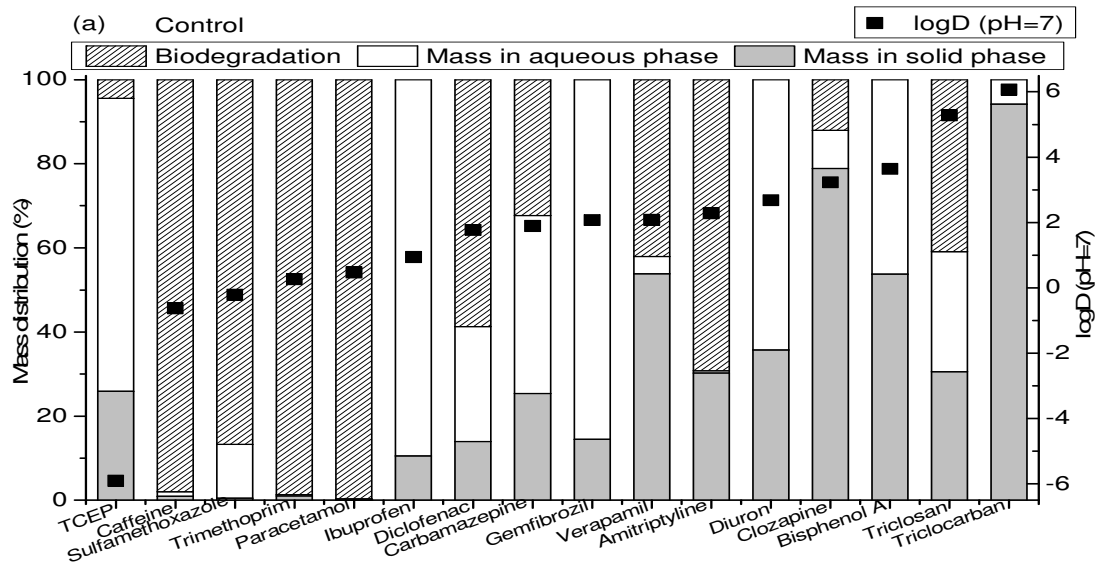
307 Fig 7 shows the fate of each TrOC amongst the three possible domain namely biodegradation,
 308 partitioning to the solid phase, and partitioning in the aqueous phase. Several readily
 309 biodegradable TrOCs can be identified from Fig 7. They include caffeine, sulfamethoxazole,
 310 trimethoprim and paracetamol (Fig 7). Likewise, four TrOCs including ibuprofen,
 311 carbamazepine, diuron and clozapine were not biodegraded under any experimental
 312 conditions in this study (Fig 7).

313 It has been established that a compound's molecular structure is a major factor governing
314 their degradability (Tadkaew et al., 2011; Wijekoon et al., 2015; Yang et al., 2016). TrOCs
315 with strong electron donating functional groups (Supplementary data Table S6) such as amine
316 (caffeine, sulfamethoxazole and trimethoprim), amino (paracetamol and sulfamethoxazole),
317 hydroxyl (paracetamol) and ether (trimethoprim) are known to be readily biodegradable. On
318 the other hand, TrOCs with strong electron withdrawing functional groups tend to be
319 persistent to biological treatment. Examples of these electron withdrawing functional groups
320 are carboxyl (gemfibrozil and ibuprofen), amide group (carbamazepine), and chloro (diuron).
321 Indeed, as can be seen in Fig 7, all TrOCs with electron withdrawing functional groups were
322 not effectively biodegraded.

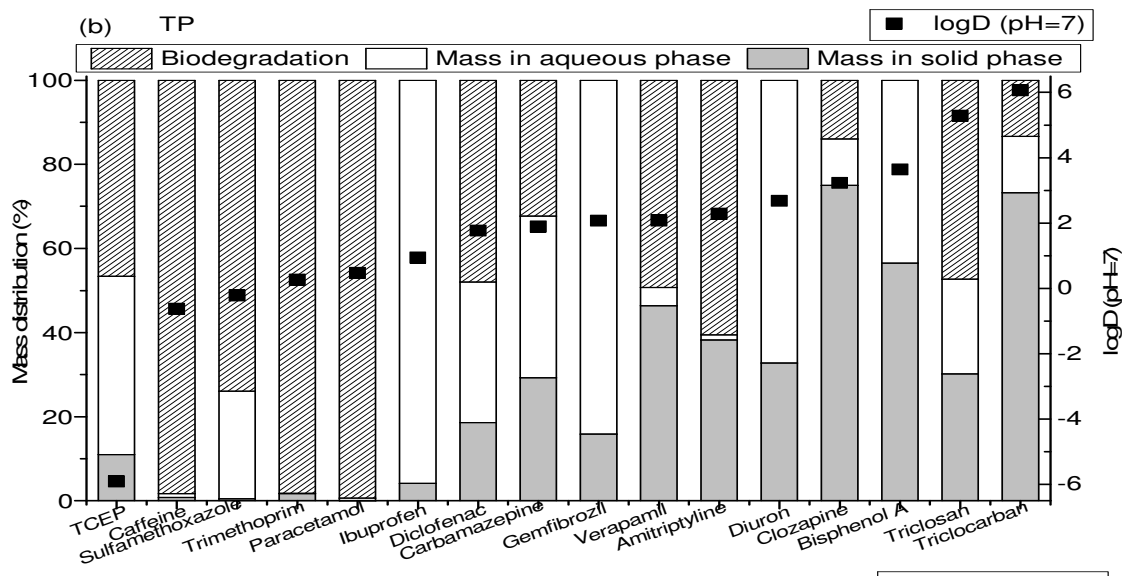
323 Results from this study are consistent with several previous studies. Caffeine (Narumiya et al.,
324 2013; Yang et al., 2016), trimethoprim (Malmborg and Magnér, 2015; Narumiya et al., 2013)
325 and sulfamethoxazole (Carballa et al., 2007; Narumiya et al., 2013) have been reported to be
326 well removed by anaerobic digestion. By contrast, carbamazepine (Carballa et al., 2007;
327 Malmborg and Magnér, 2015; Narumiya et al., 2013), diuron (Carballa et al., 2007; Tadkaew
328 et al., 2011) and ibuprofen (Alvarino et al., 2014; Malmborg and Magnér, 2015) were
329 resistant to anaerobic digestion.

330 Of particular note, enhanced biodegradation due to either thermal pre-treatment and/or
331 recuperative thickening was observed with five TrOCs (denoted in Fig 7 with #). The
332 biodegradation of triclosan and triclocarban were improved by approximately 10% due to
333 thermal pre-treatment (Fig 6a and b) and further improved (by about 15%) when recuperative
334 thickening was also applied (Fig 6c). Verapamil and clozapine were approximately 20%
335 more biodegraded when both thermal pre-treatment and recuperative thickening were
336 applied (Fig 6a and c). However, with thermal pre-treatment and recuperative thickening,
337 TCEP biodegradation increased to approximately 40% and 60%, respectively.

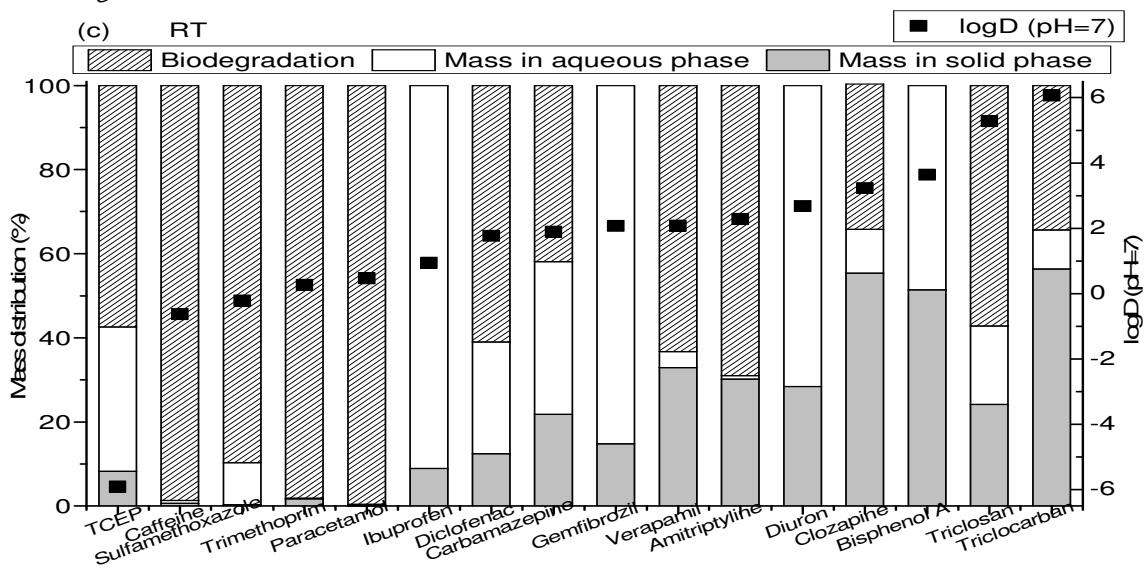
338



339



340



341 **Fig 7:** Overall fate of each compound by anaerobic digestion in digester (a) D1 (Control), (b)
 342 D2 (TP) and (c) D3 (TP+RT).

343

344 The positive impact of thermal pre-treatment and recuperative thickening does not seem to be
345 governed by the compound hydrophobicity. Indeed, of the 16 TrOCs in Fig 7, TCEP is highly
346 hydrophilic while triclosan and triclocarban are the most hydrophobic. The removal of TrOCs
347 with electron withdrawing functional groups (thus these TrOCs are inherently persistent to
348 biodegradation) is likely to benefit from thermal pre-treatment and recuperative thickening.
349 These TrOCs have at least one electron withdrawing functional group in their molecular
350 structure and are known to be persistent to biodegradation.

351 **4. Conclusions**

352 The effects of thermal pretreatment and recuperative thickening on anaerobic digestion
353 performance were examined in terms of biogas production and the removal of trace organic
354 contaminants (TrOCs). Thermal pre-treatment and recuperative thickening resulted in
355 approximately 15% increase in biogas production. In total, 16 TrOCs were detected in all
356 primary sludge samples. The effects of thermal pretreatment and recuperative thickening on
357 TrOC removal varied significantly. Removal from the aqueous phase was negligible for most
358 of the 16 TrOCs detected in the primary sludge samples. Caffeine and paracetamol were the
359 only two TrOCs with an appreciable level of removal from the aqueous phase. In comparison
360 to the aqueous phase, TrOC removal from the solid phase was considerably higher. Through
361 a mass balance calculation, it was shown that thermal pre-treatment or a combination of
362 thermal pre-treatment and recuperative thickening could enhance the biodegradation of five
363 persistent TrOCs, namely TCEP, verapamil, clozapine, triclosan, and triclocarban by 17 to
364 50%.”

365

366 **5. References**

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